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Analysis of Perchlorate in Drinking Water and Human Serum by LC-MS/MS

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Overview

The purpose of this study was to develop an LC-MS/MS method capable of detecting perchlorate (ClO_4^-) at pg/mL (ppt) concentrations in water and at ng/mL (ppb) concentrations in human serum. The current analytical method for water establishes a Method Detection Limit (MDL) of 0.53 mg/L (530 ppt) in reagent-grade water.

The data show that we can achieve MDL of ~ 15 – 20 pg/mL (ppt) in reagent-grade water. We have established accuracy and precision at fortifications ranging from 100 ppt to 2500 ppt in ground water, bottled water, surface water, tap water, and Type I water.

We have also developed a method for the detection of perchlorate in human serum. The limit of quantitation (LOQ) for this analysis, based on the lowest fortification, was 5 ppb.

Introduction

Perchlorate has been classified as an "unregulated chemical for which monitoring is required" by the State of California. The health effects of perchlorate at low dosages are still uncertain. However, in January 2002, the California Department of Health Services changed its action level from 18 µg/L (ppb) to 4 µg/L in drinking water. Perchlorate concentrations at or below 4 µg/L are not considered to pose a health concern for the public, including children and pregnant women and their developing young. However, the focus on the fetus, infant and child reflects concern about the ability of perchlorate to interfere with the production of hormones by the thyroid gland, and the need for thyroid hormones for normal prenatal and postnatal development. The Office of Environmental Health Hazard Assesment (OEHHA) is expected to draft a perchlorate Public Health Goal (PHG) in 2002.

Approved Method

The March 2, 2000 Federal Register identifies EPA Method 314.0 as the approved method for perchlorate analysis, effective January 1, 2001. This is an Ion Chromatograph (IC) method using a 1 mL sample loop.

Sources of Perchlorate Contamination

Perchlorate originates as a contaminant in ground and surface waters from the dissolution of ammonium, potassium, magnesium, or sodium salts. While ammonium perchlorate is used in solid propellant of rockets, missiles, and fireworks, perchlorate salts also have a variety of industrial uses. Perchlorate salts are used as a component of air bag inflators, in nuclear reactors and electronics, as additives in lubricating oils, in tanning and finishing leather, as a mordant for fabrics and dyes, in electroplating, aluminum refining, rubber manufacturing, the production of paints and enamels, and may be associated with certain types of fertilizers.

Sample Preparation

Most water samples did not require preparation. Samples containing sediments were filtered through a 0.44 micron HPLC filter. Serum was diluted 10x, centrifuged and filtered through a molecular sieve filter (Microcon YM).

Instrumentation

Detector: SCIEX API 3000
Interface: Turbo Ion Spray (TIS-ESI)
HPLC: HP 1100
Column: Dionex AG 16 (2mm x 50mm)
Mobile phase: A = Water, B = 50 mM NH_4OH (aq)
Flow rate: 0.8 mL/min
Injection volume: 15 µL
Ions monitored: 99 → 83 m/z, 101 → 85 m/z

Results

The MDL was calculated to be between 15 – 20 ppt in type I water, based on the response from seven fortifications at 100 ppt. The signal-to-noise ratio for the 100 ppt standard ranged between 15:1 to 20:1 (Figure 1).

The presence of perchlorate was detected in ground water, tap water, surface water, and bottled water (Table 1 and Figure 4). Levels of perchlorate ranged from approximately 50 ppt in surface water to approximately 425 ppt in ground water. Perchlorate was not found in type I water generated on-site.

Excellent accuracy and precision were observed at fortifications ranging from 100 ppt to 2500 ppt in ground water, bottled water, surface water, tap water, and type I water (Table 2). The overall percent recovery for all the fortifications (n = 50) was 99.7% with a standard deviation of 6.1%. Monitoring the transition 101 → 85 m/z can be used as an additional confirmation of the perchlorate ion (Figure 5). Excellent linearity was observed for perchlorate standards in water ranging from 100 to 2500 ppt (Figure 6).

The MDL for perchlorate in serum was approximately 2.0 ppb, based on standards prepared in matrix. The signal-to-noise ratio for the 5 ppb standard prepared in human serum was approximately 12:1 (Figure 2).

Results, cont.

The average recovery for perchlorate in serum samples fortified at concentrations ranging from 5 to 100 ppb was 88.2% with a SD of 10.6% (Table 3). Monitoring the transition 101 → 85 m/z can be used as a additional confirmation of the perchlorate ion (Figure 3). Excellent linearity was observed for perchlorate standards prepared in human serum, ranging from 5 to 100 ppb (Figure 7).

Conclusions

The use of LC-MS/MS analysis helped achieve lower detection limits. The MDL in water achieved in this study (15 to 20 ppt) is 25-fold lower than the currently approved method. Concentrations as low as 5 ppb perchlorate can be detected and quantitated in human serum. The transition from 101 → 85 m/z resulting from the ^{37}Cl ion can be used as a confirmatory ion, if needed.

Table 1

Summary of perchlorate found in water samples.

Source	Sample	Perchlorate Found (ppt)
Ground Water*	Sample	418
	Duplicate	425
Bottled Water	Sample	150
	Duplicate	156
Surface Water*	Sample	52
	Duplicate	49
Tap Water*	Sample	249
	Duplicate	256
Type I Water	Sample	< MDL**
	Duplicate	< MDL**

*Obtained from State College, PA **MDL = 15 to 20 ppt

Table 2

Fortification recoveries (%) for perchlorate in water.

Spike level (ppt)	Ground Water	Bottled Water	Surface Water	Tap Water	Type I Water
100 Spk A	91.7	107.3	107.2	95.3	97.8
100 Spk B	116.9	104.4	98.3	111.2	97.2
200 Spk A	106.4	95.0	96.9	107.6	96.4
200 Spk B	111.9	107.7	103.7	100.2	102.1
500 Spk A	100.3	98.1	96.6	92.1	92.4
500 Spk B	99.4	95.4	94.8	93.7	99.9
1000 Spk A	98.9	97.1	93.9	95.3	96.4
1000 Spk B	97.9	95.2	95.8	96.0	97.8
2500 Spk A	96.9	96.3	95.3	98.6	96.3
2500 Spk B	106.6	117.6	94.2	100.5	101.0
Mean	102.7	101.3	97.7	99.1	97.2
Std Dev	7.6	7.7	4.4	6.1	2.8

Table 3

Fortification recoveries (%) for perchlorate in human serum.

	5 ppb	10 ppb	25 ppb	50 ppb	100 ppb
Spike 1	98.6	86.5	90.3	88.7	86.8
Spike 2	80.2	88.3	72.8	91.2	106.6
Spike 3	77.6	86.6	—	89.1	98.8
Spike 4	99.0	76.5	—	65.0	—
Spike 5	—	75.4	—	100.8	—
Spike 6	—	101.8	—	93.7	—
Mean	88.8	85.9	81.6	88.1	96.4
Std Dev	9.58	9.96	8.18	6.07	9.9

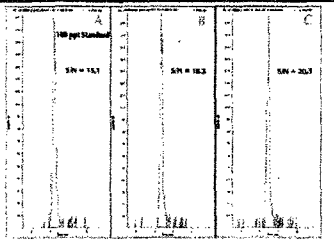

Figure 1
Repeat injections of a 100 ppt perchlorate standard in water.
99 → 83 m/z, S/N > 15:1

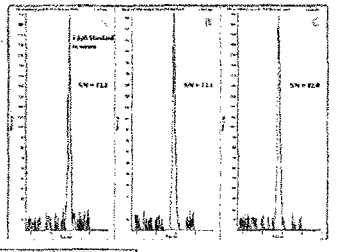

Figure 2
Repeat injections of a 5 ppb perchlorate standard in human serum.
99 → 83 m/z, S/N > 12:1

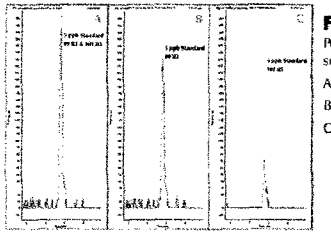

Figure 3
Perchlorate 5 ppb standard in serum
A) Total Ion Chromatogram (TIC)
B) 99 → 83 m/z
C) 101 → 85 m/z

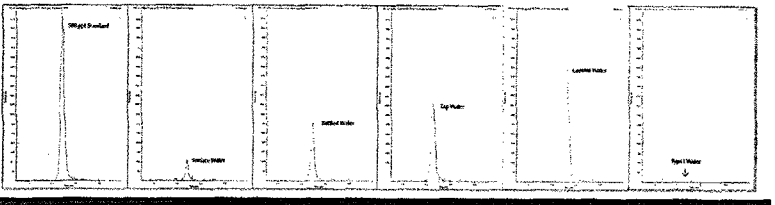

Figure 4
Perchlorate in (A) 500 ppt perchlorate standard, (B) surface water, (C) bottled water, (D) tap water, (E) ground water, and (F) type I water.
99 → 83 m/z

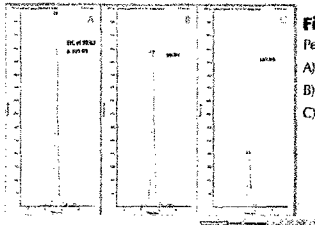

Figure 5
Perchlorate in ground water.
A) TIC
B) 99 → 83 m/z
C) 101 → 85 m/z

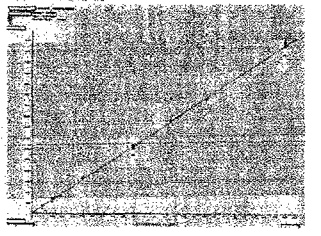

Figure 6
Calibration curve for perchlorate in type I water.
100 ppt to 2500 ppt
R^2 = 0.997

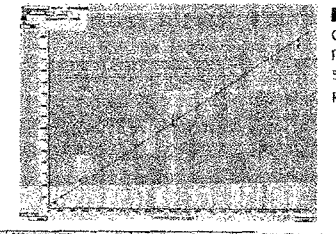

Figure 7
Calibration curve for perchlorate in human serum.
5 ppb to 100 ppb
R^2 = 0.995

References
California Department of Health Services: www.dhs.ca.gov/ps/ddwem/chemicals/perchl/perchlindex.htm
EPA Office of Water: www.epa.gov/OGWDW/methods/met314.html